

On the suitability of high vacuum electrospray deposition for the fabrication of molecular electronic devices

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Abstract

We present a series of three studies investigating the potential application of high vacuum electrospray deposition to construct molecular electronic devices. Through the use of time of flight secondary ion mass spectrometry we explore the use of this novel deposition technique to fabricating multilayer structures using materials that are compatible with the same solvents and films containing a mixture of molecules from orthogonal solvents. Using x-ray photoelectron spectroscopy we study the deposition of a polymer blend using electrospray and find evidence of preferential deposition of one of the components.

Keywords: Electrospray Deposition, ToF-SIMS, XPS, Molecular Electronics, Polymers

1. Introduction

Vacuum electrospray deposition (ESD) is an emerging technique that has allowed researchers to study complex molecules on surfaces, *in-situ*, using a vast array of analytical techniques requiring high vacuum including various photoemission[1, 2, 3] and scanning probe techniques[4, 5]. Early examples of work using high vacuum ESD studied the bonding of molecules used in dye sensitised solar cells such as the benchmark N3 sensitiser dye on the titanium dioxide surface[1]. The technique has also been applied beyond

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Preprint submitted to Chemical Physics Letters

May 24, 2017

9 traditional surface science experiments and used with biological systems[6,
10 7]. In recent years molecular photovoltaics, such as organic solar cells, are
11 increasingly reliant on the construction of multilayer and bulk heterojunction
12 structures[8, 9]. Ambient electrospray deposition has been used as a tool
13 to construct such structures[10] providing a pathway to use high vacuum
14 electrospray to study critical parts of such devices *in-situ*.

15 Electrospray deposition relies on the formation of a beam of molecular
16 ions via the electrospray ionisation process. This has been thoroughly dis-
17 cussed elsewhere[11, 12, 13], but in summary, a fluid is passed through a
18 small capillary tube with a large voltage (\sim kV) applied to it. The voltage
19 causes the liquid emerging from the capillary to be drawn into a well-defined
20 shape known as a Taylor cone - at the tip of which the charge on the liquid
21 is so high a jet of liquid is expelled. Due to the charge on the liquid's sur-
22 face, the jet pinches off into a stream of droplets which in turn repeatedly
23 fission into ever smaller drops. This plume of ionised droplets can be fired
24 into a differentially pumped vacuum system where a series of apertures al-
25 low the pressure to be reduced to high vacuum conditions whilst skimming
26 the ionised droplets, from which solvent is evaporating, into a narrowly di-
27 verging beam of molecular ions. Placing a surface in the path of this beam
28 allows a film of the solute to be grown on the surface with minimal solvent
29 contamination.

30 2. Instrumentation

31 The ESD system used was a Molecularspray UHV4 (a schematic is shown
32 in Figure 1a). This portable deposition source consisted of a 250 μ m inlet
33 capillary, 0.4 mm and 0.6 mm skimmer cones separating the first two vac-
34 uum stages (pumped using roughing pumps) from the 3rd vacuum stage
35 pumped using a turbomolecular pump. The exit from the instrument was
36 a 1 mm aperture. The deposition chamber, pumped using a turbomolecular
37 pump, had a base pressure of 1×10^{-7} mbar and a deposition pressure of
38 1×10^{-6} mbar. The depositions were monitored by observing fluctuations in
39 the pressure and the inlet capillary was flushed regularly (with the valve to
40 the deposition chamber closed) to avoid clogging/blockages from the sprayed
41 molecules.

42 The solutions were fed into the emitter capillary (New Objective Stainless
43 Steel TaperTip) by a syringe pump delivering a flow rate of 0.3 ml h^{-1} . Before
44 each deposition the emitter, syringe and tubing were thoroughly flushed with

45 solvent. A bias of ~ 2 kV was applied to the emitter with respect to the
46 grounded entrance capillary.

47 Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used as
48 an imaging technique. ToF-SIMS utilises ion sputtering to lift fragments off
49 the surface whilst a time of flight mass spectrometer measures mass spectra of
50 the fragments. These spectra can be collected as a function of time and/or
51 space in the x,y plane of the sample. This allows chemical maps of the
52 sample to be constructed, in which each pixel represents a full mass spectrum,
53 making it the ideal technique for imaging sub millimetre structures with
54 chemical contrast. The instrument used was an ToF-SIMS IV instrument
55 (IONTOF GmbH) with a 25 keV Bi primary ion source (with a Bi_3^+ cluster
56 beam applied). The primary ion dose was kept below the static limit and an
57 electron flood gun (< 20 eV) was used to prevent charging.

58 X-ray photoelectron spectroscopy (XPS) was used to provide chemical
59 analysis of thin films and bulk samples. By irradiating a sample with x-
60 ray photons, electrons are emitted from the sample into the vacuum (the
61 photoelectric effect). By measuring the kinetic energy of these emitted pho-
62 toelectrons, the original binding energy of the electrons can be determined
63 meaning XPS is sensitive to the chemical environment of electrons. XPS
64 therefore allows quantitative measurements of blends of molecules that may
65 contain the same elements existing in different chemical states, and due to its
66 high surface sensitivity (limited to the nanometre range by the escape depth
67 of the photoelectrons), XPS is ideal for studying the chemistry of thin films.
68 In this study, a Kratos Axis Ultra instrument was used with a monochromo-
69 tised aluminium $K\alpha$ x-ray source. Charge neutralisation was provided using
70 an electron flood gun. The analyser was set to measure in hybrid mode with
71 a pass energy of 20 eV.

72 The molecules and solutions used for each of the three experiments are
73 detailed in their respective sections. All were purchased from Sigma Aldrich.

74 3. Methods, results and discussion

75 3.1. Layered deposits of molecules from the same solvent

76 Multilayer structures of different organic materials are critical in the con-
77 struction of a range of devices including Bragg reflectors[14], photovoltaic
78 devices such as organic solar cells[8], and drug delivery systems[15]. Tech-
79 niques like spin casting provide the capability to build high quality multilayer

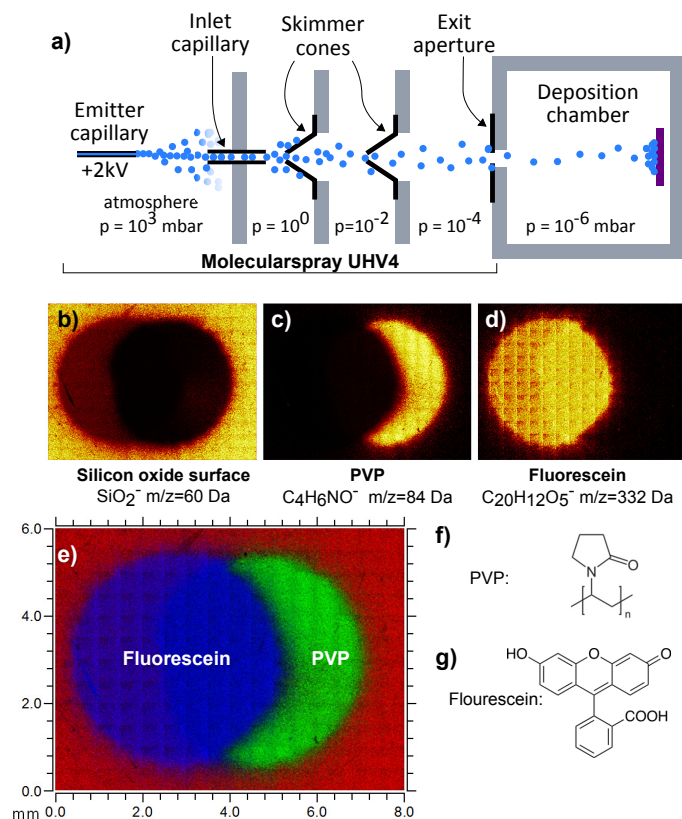


Figure 1: a) Schematic of the Molecularspray UHV4 system used to fabricate bi-layer structures. b-d) ToF-SIMS images built using markers for SiO_2 , PVP and fluorescein respectively. e) Composite image using the above 3 markers shown in red, green and blue respectively. f-g) chemical structure of PVP and fluorescein.

structures from molecules that are compatible with different solvents: Bailey et al have shown, using ToF-SIMS, that alternate spin cast layers of polystyrene (PS) and polyvinylpyrrolidone (PVP) dissolved in toluene and water respectively, can produce multilayer structures that have highly repeatable layer thickness and sharp interfaces[16]. However, these traditional wet chemistry preparation methods are limited to the use of materials dissolved in orthogonal solvents (solvents that will dissolve one species but not another). Solvent free techniques, such as electrospray deposition, provide a potential solution to overcoming this experimental limitation.

A silicon wafer substrate was cleaned via ultrasonication in acetone, methanol and isopropanol. Thin films of polyvinylpyrrolidone (PVP), with

91 an average molecular weight 360 kDa, followed by fluorescein dye were de-
92 posited at room temperature using electrospray onto the native oxide surface.
93 Both molecules were dissolved in methanol to a concentration of 0.1 % (w.t)
94 and further diluted to 0.05 % (w.t) for deposition. Each deposition lasted an
95 hour and the sample, which was held on a transfer arm 0.5 m away from the
96 exit aperture of the UHV4, was moved slightly between depositions; both
97 depositions were therefore visible but with an overlapping area.

98 ToF-SIMS was used to image this fluorescein/PVP bi-layer on the silicon
99 oxide surface. Figure 1b-d shows secondary ion images constructed from
100 the intensity of individual peaks in the mass spectra selected as markers
101 for the surface and each molecule. The spectral values used as markers for
102 the oxide surface, PVP and fluorescein were 60 Da, 332 Da and 84 Da.
103 A composite image showing the intensity of the different markers is also
104 included in Figure 1e. These images show there is minimal mixing between
105 the layers where the fluorescein film appears on top of the PVP deposit
106 eclipsing the image of the PVP (Figure 1c) with little signal attributed to
107 the PVP in the overlapping region. Although, the depositions were very
108 thin, some preliminary depth profiling experiments illustrated the presence
109 of underlying PVP in the overlapping region (data not shown).

110 3.2. Deposition of immiscible polymer blends

111 Producing a film containing a blend of molecules from orthogonal solvents
112 can be an experimentally challenging problem. Electrospray deposition pro-
113 vides a potential solution; as there should be minimal amounts of solvent,
114 simultaneous depositions of the two molecules from different electrospray
115 sources should allow the mixing of the molecules at the surface. This was
116 attempted using the setup shown in Figure 2a. Two electrospray sources,
117 of the type used in section 3.1, were placed at 90° to each other with the
118 sample at 45°. The sources were 8 cm from the surface. It was not possible
119 to monitor the pressure in the chamber during deposition but the system was
120 allowed to pump down sufficiently that the ultimate deposition pressure of
121 $\sim 1 \times 10^{-6}$ mbar was achieved.

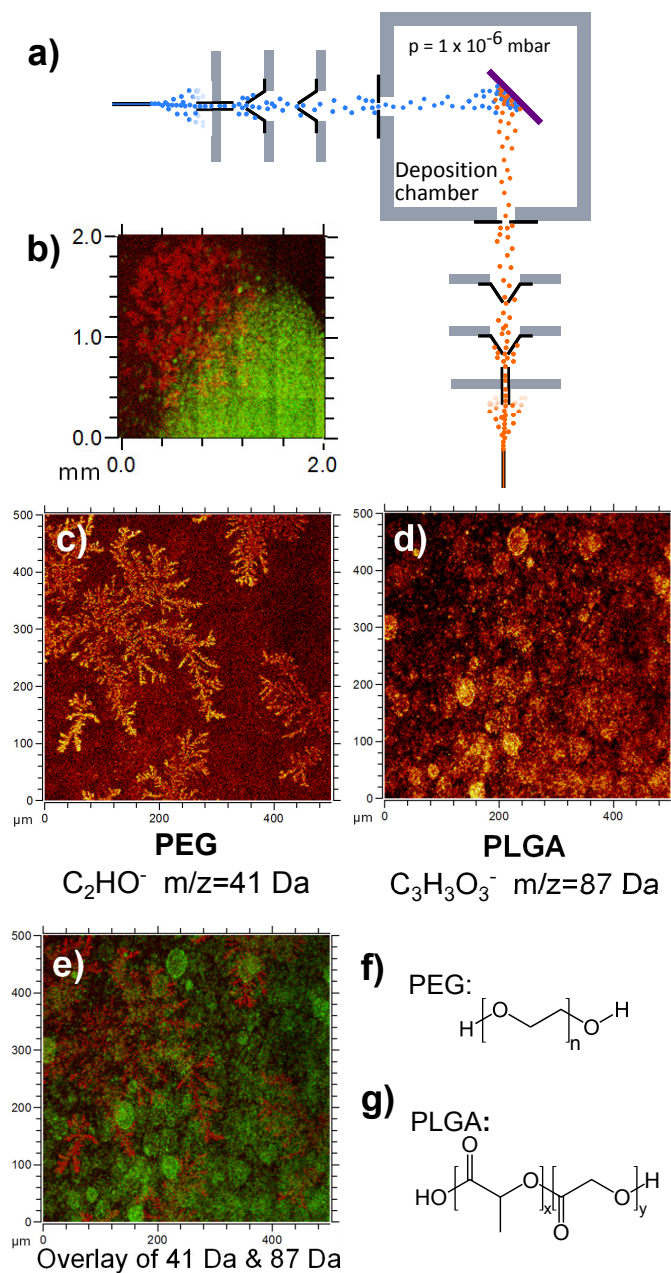


Figure 2: a) Geometry used to co-deposit molecules from two solutions using two MolecularSpray UHV4 systems. b) ToF-SIMS composite image showing the markers for PEG (red) and PLGA (green). c-e) high resolution images of the overlap region for each of the two markers a composite respectively. f-g) show the chemical structure of PEG and PLGA.

122 The two polymers used were poly(lactic-co-glycolic acid) (PLGA) and
 123 Polyethylene glycol (PEG) dissolved in acetone and methanol respectively
 124 to a concentration of 0.1 % (w.t.). The PLGA, a co-polymer with average
 125 molecular weight between 40 kDa and 75 kDa, had a ratio of 65:35 for the
 126 lactide:glycolide monomer components. The PEG had a molecular weight
 127 of 3.35 kDa. PLGA and PEG were co-deposited at room temperature for
 128 around 1 hour onto a clean silicon wafer (ultrasonicated in acetone, methanol
 129 and isopropanol) and the resulting deposition was imaged using ToF-SIMS.
 130 A sample of the images collected are shown in Figure 2. The two diagnos-
 131 tic secondary ions used are $m/z = 41$ (C_2HO^-) for PEG and $m/z = 87$
 132 ($\text{C}_3\text{H}_3\text{O}_3^-$) for PLGA. A 2 mm area overlay image is shown in Figure 2b il-
 133 lustrating the overlapping deposits. A 500 μm area within the overlap region
 134 is shown for the PEG and PLGA markers and as an overlay in Figures 2c
 135 2d and 2e respectively. Secondary ion images were also measured away from
 136 the overlapping region in areas containing each individual species. The mor-
 137 phologies of which showed comparable structure to that of the overlapping
 138 region.

139 Firstly it is clear that in the overlapping region there has been some
 140 mixing of the two components. The PEG has also formed a large scale fractal
 141 structure on the surface. This behaviour implies the molecule is mobile on the
 142 surface, which, considering the size of the PEG polymer chains, implies there
 143 is likely a small amount of solvent on the surface allowing such structures to
 144 form. The same argument could also be made for the “blob” like structure
 145 of the PLGA. Despite this, an immiscible polymer blend has been achieved
 146 on the surface with domain sizes on the micron length scale.

147 Although acetone and methanol are miscible, when the two solutions
 148 were mixed, the mixture turned cloudy as the molecules partially drop out
 149 of solution. The same experiment does however have the potential to be
 150 applied to completely immiscible polymer solutions, for example those soluble
 151 exclusively in water and toluene.

152 3.3. Miscible polymer blends for organic photovoltaics

153 The polymer blend PEDOT:PSS is used in organic photovoltaic devices as
 154 a hole conducting layer. It contains a mixture of poly(3,4-ethylenedioxythiophene)
 155 and polystyrene sulfonate as shown in Figure 3d and 3e. Here we use XPS to
 156 compare films of PEDOT:PSS deposited using electrospray deposition and
 157 the more traditional spin casting directly from solution.

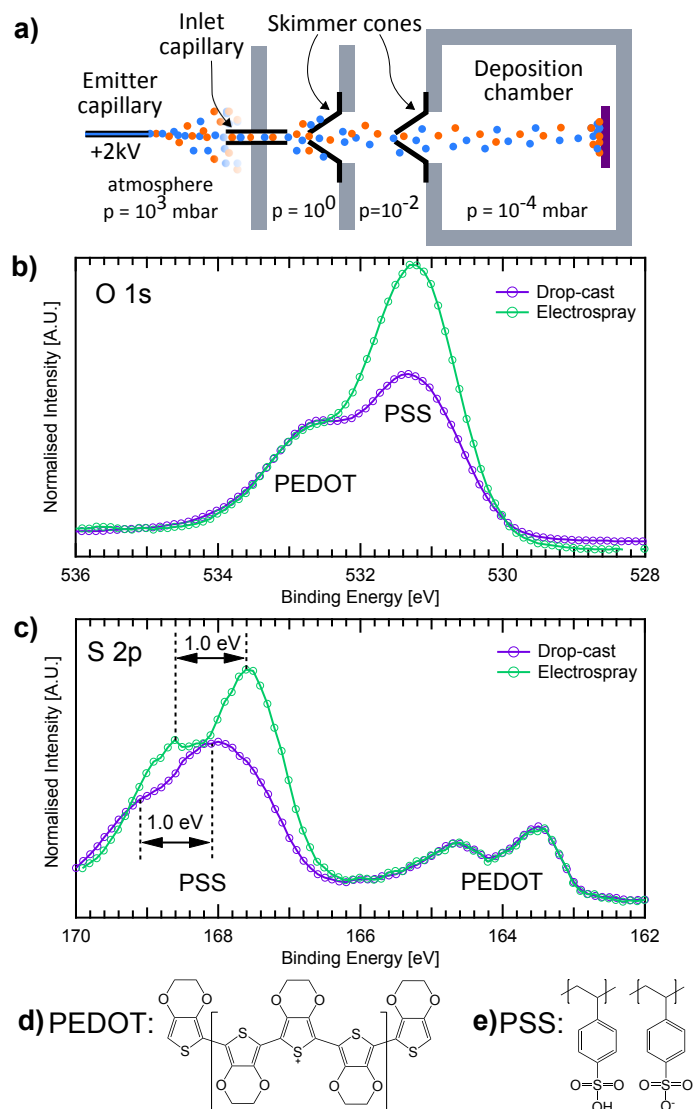


Figure 3: a) The electrospray deposition source used to deposit PEDOT:PSS consisted of one less pumping stage than the UHV4 source used in the previous sections. b-c) show O 1s and S 2p XPS measurements for an electrospray deposited sample and a drop cast sample of the same solution. d-e) show the two components of the PEDOT:PSS polymer blend. PSS is a co-polymer of the two groups shown.

Gold substrates were made by thermally evaporating 10 nm of titanium and 100 nm gold onto silicon wafer. The titanium was used to improve cohesion between the gold film and the silicon oxide surface. The silicon wafer was cleaned by ultrasonication in acetone, methanol and isopropanol prior to evaporation. PEDOT:PSS (Orgacon dry re-dispersible pellets by Agfa) was dissolved in deionised water and drop cast onto one substrate. This solution was diluted to 0.01 % (w.t.) and electrosprayed onto another substrate using the apparatus shown in Figure 3a. Both experiments were carried out with the substrates at room temperature. This apparatus contained one fewer pumping stage than the Molecularspray UHV4 (as used in Sections 3.1 and 3.2) to maximise deposition flux as low pressures and desolvation were less critical. 10 % methanol added to the solution to improve the quality of the spray.

Figures 3b shows XPS measurements of the O 1s region for both the drop cast and electrospray deposition samples (both were prepared *ex-situ*). The O 1s spectra contains two overlapping peaks with binding energies of 532.8 eV and 531.3 eV. We have attributed the higher binding energy peak to the ethylenedioxy attachment to the thiophene ring of the PEDOT and the lower binding energy peak to the sulfonate side group of the PSS. Both spectra have been normalised to the PEDOT/thiophene shoulder. There is a clear increase of the PSS/sulfonate contribution for the electrosprayed sample.

Figure 3c shows XPS spectra of the S 2p region (measured at the same position on both samples as the O 1s data). There are two doublets in the spectra resulting from the spin orbit splitting of the 2p states of sulphur in the PEDOT and PSS molecules. We have attributed the lower binding energy doublet, centred at approximately 164 eV, to the PEDOT's thiophene ring and the much broader feature at higher binding energy, centred at approximately 168 eV, to the sulfonate group of the PSS. Again, both spectra are normalised to the PEDOT contribution and there is a clear increase in PSS signal for the electrosprayed sample.

The broadening and binding energy shift of the sulfonate peaks of the drop cast relative to the ESD sample is attributed to charging effects due to the thickness of the drop cast deposit. We suspect that this is only present in the PSS and not the PEDOT as the PEDOT is a fully conjugated conductive polymer. Measurement at different sample positions shows the same feature shapes and there was no sign of beam damage between the start and end measurements at a single position.

196 It is worth noting that the two polymers in the PEDOT:PSS blend are
197 individually charged. As shown in Figures 3d 3e, PEDOT has positive
198 charges on the thiophene backbone whilst PSS has negatively charged sul-
199 fonate groups. It is possible this could explain why the electrospray technique
200 would preferentially deposit one species over the other - however in this case
201 the experiment was carried out in the positive bias mode and we are see-
202 ing potential preferential ionisation of the negative species which is counter
203 intuitive.

204 Analysis of the C 1s was hindered by atmospheric carbon contamination
205 (during transport of the samples from the deposition apparatus to the XPS
206 instrument) so is not included here. Carbon spectra were used to provide
207 relative calibration between the two samples where the low binding energy
208 edge of the C 1s region implies a 0.9 eV shift between the two samples. This
209 offset was applied to all the included spectra.

210 4. Summary and conclusions

211 Three experiments have been presented highlighting the capabilities and
212 potential challenges of using electrospray to produce multi-layered structures
213 and blends of materials. Firstly we have shown that the solvent contamina-
214 tion on the surface is low enough to build up thin layers of molecules that are
215 compatible with the same solvents without substantial mixing of the films.
216 However, ultra high vacuum compatible electrospray deposition is not well
217 suited to building up thick deposits and although SIMS is surface sensitive
218 enough to measure surface coverage, conventional sputtering does not allow
219 depth profiling of such thin films (when probed with XPS we find similar
220 deposits are several monolayers thick). With the co-deposition experiment
221 we have shown there is almost certainly a small solvent contribution to the
222 deposit allowing structure to form on the surface. More sophisticated electro-
223 spray instruments have applied techniques such as mass selection and heated
224 inlet capillaries to attempt to combat these issues.

225 The XPS analysis of the PEDOT:PSS blend is of importance and certainly
226 needs further study. It appears as though the electrospray deposition process
227 preferentially ends up with one species over another being ionised, entering
228 the vacuum system and landing on the surface. Although we have shown with
229 SIMS that a simple vacuum compatible electrospray source can be utilised
230 to build the sort of films used in molecular devices, care should be taken if
231 simultaneously depositing multiple species.

5. Acknowledgements

The authors are grateful for technical support from Emily Smith at Nottingham's Nanoscale and Microscale Research Centre (NMRC) XPS facility. Equipment access was funded by University of Nottingham Interdisciplinary Center for Analytical Science (UNICAS) and Advanced Molecular Materials Research Priority Area. Further funding was provided by EPSRC and Molecularspray Ltd through a DTG/CASE conversion studentship, and a Nottingham University discipline bridging award.

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